

PATENT SPECIFICATION

(11)

1 496 832

1 496 832

- (21) Application No. 18370/75 (22) Filed 2 May 1975
 (61) Patent of Addition to No. 1 444 799 dated 7 Dec. 1973
 (31) Convention Application No.
 2 421 406 (32) Filed 3 May 1974 in
 (33) Federal Republic of Germany (DE)
 (44) Complete Specification published 5 Jan. 1978
 (51) INT. CL.² C07D 307/79
 (52) Index at acceptance
 C2C 1474 213 247 253 25Y 296 297 305 30Y 351 352 369
 386 409 46Y 635 761 TQ

(19)



(54) PROCESS FOR THE OXIDATION OF *O*-XYLENE
 NAPHTHALENE TO PHTHALIC ANHYDRIDE

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Our copending British Patent Application 10 56,865 (Serial No. 1 444 799) describes and claims a supported catalyst for the oxidation of *o*-xylene or naphthalene to phthalic anhydride, comprising an inert non-porous carrier and applied thereto a layer of catalytically active material which contains from 15 1 to 40 per cent by weight of vanadium pentoxide and from 60 to 99 per cent by weight of anatase and which has a vanadium pentoxide content of from 0.05 to 4 20 per cent by weight based on the supported catalyst, wherein the catalytically active material contains from 0.01 to 0.15 per cent by weight, based on anatase, or sodium or potassium in the form of a compound devoid 25 of sulfur.

We have found that the supported catalysts claimed in the above application may be modified so that the catalytically active material contains, in place of the sodium or 30 potassium, from 0.01 to 0.15 per cent by weight, based on anatase, of rubidium or caesium in the form of a compound devoid of sulfur, and that the resulting catalysts give advantageous results when used as 35 catalysts in the manufacture of phthalic anhydride by oxidation of *o*-xylene or naphthalene with molecular oxygen.

In manufacturing the catalysts, the alkali metals are added to the catalytic material as 40 sulfur-free compounds, for example as oxides or other oxygen-containing compounds, such as carbonates or acetates.

In other respects, the statements in the above patent application apply.

45 The following Examples illustrate the

present invention. The steatite spheres used as carrier for the supported catalyst are non-porous, and inert.

Example 1

1,800 g of steatite spheres of 6 mm diameter are heated to 300°C in a coating drum. The hot spheres are sprayed, whilst maintaining the above temperature, with a suspension consisting of 400 g of finely 55 ground alkali-free anatase having an internal surface area of 11 m²/g, 42.2 g of vanadyl oxalate in 400 ml of water, 140 ml of formamide, 200 ml of water and 0.58 g of rubidium carbonate until they have taken 60 up 6% by weight of catalytic material.

The catalytic material contains 93.89% by weight of anatase, 6% by weight of pentoxide and 0.11% by weight of Rb₂O, corresponding to 0.10% by weight of rubidium. 65

The catalyst is introduced into a tube of 25 mm internal diameter and 3 m length, surrounded by a salt bath. 5,000 liters (S.T.P.) of air per hour are passed through the catalyst bed. Using a salt bath temperature of 375°C and charging the air with 40 g of *o*-xylene per cubic meter (S.T.P.), the yield is 109% by weight of phthalic anhydride, based on 100% pure *o*-xylene, after 40 days' operation, 110% by weight 75 after 55 days and 111% by weight after 80 days.

Example 2

1,800 g of steatite spheres of 6 mm diameter are heated to 300°C in a coating drum. The hot spheres are sprayed, whilst maintaining the above temperature, with a suspension consisting of 400 g of finely 80 ground alkali-free anatase having an internal surface area of 11 m²/g, 42.2 g of vanadyl oxalate in 400 ml of water, 140 ml of formamide, 200 ml of water and 0.40 g of caesium carbonate until they have taken up 85 6.0% by weight of catalytic material. 90

The catalytic material contains 93.92% by weight of anatase, 6.0% by weight of vanadium pentoxide and 0.08% by weight of Cs_2O , corresponding to 0.076% by weight of caesium.

The catalyst is introduced into a tube of 25 mm internal diameter and 3 m length, surrounded by a salt bath. 5,000 litres (S.T.P.) of air per hour are passed through the catalyst bed. At a salt bath temperature of 380°C and charging the air with from 40 to 42 g of *o*-xylene/cubic meter, a yield of 109.5% by weight of phthalic anhydride, based on 100% pure *o*-xylene, is obtained.

It is proposed in copending UK patent application No. 46722/72 (Serial No. 1391313) to manufacture phthalic anhydride by vapor phase catalytic oxidation of either ortho-xylene or naphthalene with a molecular oxygen-containing gas, comprising a catalytically active substance supported on a porous inert carrier having an apparent porosity of at least 10% and certain other characteristics, the catalytically active substance comprising 1 to 20 parts by weight of V_2O_5 and correspondingly 99 to 80 parts by weight of TiO_2 and, based on the total weight of the V_2O_5 and TiO_2 , 0.02 to 5.0% by weight of Nb_2O_5 , 0.1 to 5.0% by weight of P_2O_5 , 0 to 0.25% by weight of K_2O and 0 to 0.5% by weight of Cs_2O , the total weight of K_2O plus Cs_2O being at least 0.05%. By contrast the process of the present invention employs a non-porous inert carrier for the supported catalyst it uses.

Having regard to the provisions of Section 9 of the Patents Act, attention is directed to Patent No. 1 409 377.

40

WHAT WE CLAIM IS:—

1. A process for the catalytic oxidation of *o*-xylene or naphthalene with molecular oxygen to form phthalic anhydride, wherein a supported catalyst is used comprising an inert non-porous carrier and applied thereto a layer of catalytically active material which contains from 1 to 40% by weight of vanadium pentoxide and from 60 to 99% by weight of anatase and which has a vanadium pentoxide content of from 0.05 to 4% by weight based on the supported catalyst, wherein the active material contains

from 0.01 to 0.15% by weight, based on anatase, of rubidium or caesium in the form of a compound devoid of sulfur.

2. A process as claimed in claim 1 wherein the catalytically active material constitutes from 3 to 10% by weight of the supported catalyst.

3. A process as claimed in claim 1 or 2 wherein the anatase in the supported catalyst has an internal surface area of from 8 to 15 m^2 per gram.

4. A process as claimed in any of claims 1 to 3 wherein the carrier of the supported catalyst is in the form of spheres having a diameter of from 4 to 12 mm.

5. A process as claimed in any of claims 1 to 4 wherein the anatase in the supported catalyst has a particle size of less than 1 micron.

6. A process as claimed in claim 5 wherein the anatase in the supported catalyst has a particle size of from 0.4 to 0.8 micron.

7. A process as claimed in any of claims 1 to 6 wherein the catalytically active material of the supported catalyst additionally contains from 0.1 to 3% by weight of phosphorus in the form of a compound.

8. A process as claimed in any of claims 1 to 7 wherein the catalytically active material of the supported catalyst contains from 0.1 to 15% by weight of an oxide of aluminum, zirconium, antimony, arsenic, niobium, chromium, molybdenum, tungsten, cobalt or nickel.

9. A process as claimed in any of claims 1 to 8 wherein the layer of catalytically active material on the carrier in the supported catalyst has a thickness of from 0.04 to 0.2 mm.

10. A process for the manufacture of phthalic anhydride carried out substantially as described in the foregoing Example 1 or Example 2.

11. Phthalic anhydride when manufactured by a process as claimed in any of claims 1 to 10.

J. Y. & G. W. JOHNSON,
Furnival House,
14-18 High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.